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Utilising Sodium-Mediated Ferration for Regioselective Functionalisation of Fluoroarenes via C-H and C-F Bond Activations

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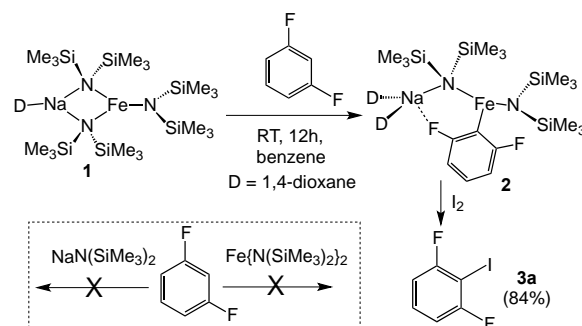
Abstract: Pairing iron bis(amido) $\text{Fe}(\text{HMDS})_2$ with $\text{Na}(\text{HMDS})$ to form new sodium ferrate base $[(\text{dioxane})_{0.5}\text{NaFe}(\text{HMDS})_3]$ (**1**) enables regioselective mono and di-ferration (via direct Fe-H exchange) of a wide range of fluoroaromatic substrates under mild reaction conditions. Trapping of several ferrated intermediates has provided key insight into how synchronised Na/Fe cooperation operates in these transformations. Furthermore using excess **1** at 80°C switches on a remarkable cascade process inducing the collective 2-fold C-H/3-fold C-F bond activations, where each C-H bond is transformed to a C-Fe bond whereas each C-F bond is transformed into a C-N bond.

Attracted by low cost, high natural abundance and low toxicity of the metal, organoiron chemistry continues to expand as increasing focus is directed towards sustainable practices. Though iron complexes have demonstrated proficiency in a myriad of cornerstone organic bond forming transformations under both stoichiometric and catalytic regimes, an area that remains surprisingly scant is deprotonative metallation.^[1] Metal-hydrogen exchange (metallation) is one of the World's most practiced reactions.^[2] Alkylolithium or lithium amide reagents dominated metallation for decades, but recently new bimetallic systems have gained prominence as more efficient, more chemoselective alternatives.^[3] Only limited advances have been made in direct ferration of aromatic molecules. For example, Mongin used an *in situ* 1:3, $\text{FeBr}_2\text{:LiTMP}$ stoichiometry for ferration of substituted pyridines, though Fe(II)/Fe(III) or Fe(II)/Fe(IV) couples were proposed to interfere, leading to homocoupling side reactions.^[4] Knochel similarly prepared trimetallic $(\text{TMP})_2\text{Fe}\cdot 2\text{MgCl}_2\cdot 4\text{LiCl}$ *in situ* to ferrate a range of functionalised arenes to form diaryl Fe(II) compounds.^[5] Significantly, the identities of the iron intermediates involved in this challenging chemistry were not identified. A case where structural elucidation proved possible was Mulvey's regioselective 2-fold ferration of benzene at the 1,4-positions by the sodium ferrate $[(\text{TMEDA})\text{NaFe}(\text{TMP})_2(\text{CH}_2\text{SiMe}_3)]$, which affords an iron-host inverse crown complex.^[6]

While iron bis-amide, $\text{Fe}(\text{HMDS})_2$ [$\text{HMDS} = \text{N}(\text{SiMe}_3)_2$], has been reported as a useful precursor to access low-coordinate Fe complexes,^[7] the low polarity of its Fe-N bonds makes it, *a priori*, unsuitable for C-H metallation applications. Breaking new ground in this field, by pairing this seemingly toothless base with

its sodium congener, we disclose (i) a new methodology for regioselective functionalisation of fluoroarenes which occurs via direct ferration of these aromatic scaffolds, and (ii) an unprecedented ate-mediated C-F bond activation process for C-N bond conversion.

While naturally occurring fluoroarenes are rare, synthetic forms are extremely valuable building blocks. Thus developing methods allowing the incorporation of these units into more complex molecular scaffolds is highly important.^[8] Interestingly, deprotonation of these molecules via organolithium bases still remains a challenge, primarily due to the exceptionally fragile stability of generated intermediates, which even at cryogenic conditions can eliminate LiF , to form benzyne intermediates as well as engaging in complex cascade processes involving autometallation.^[9] Also, even when low polarity metallators are used, fluoride elimination cannot be halted as shown recently by our group on alumination of fluoroarenes using *trans-metal-trapping* Li/Al combinations, where metallated products decompose at room temperature.^[10]



Scheme 1. Sodium-mediated ferration of 1,3-difluorobenzene by $[(\text{dioxane})_{0.5}\text{NaFe}(\text{HMDS})_3]$ (**1**)

We started the study by preparing the sodium tris(amido)ferrate $[(\text{dioxane})_{0.5}\text{NaFe}(\text{HMDS})_3]$ (**1**) in an isolated crystalline yield of 64% by co-complexing $\text{Na}(\text{HMDS})$, $\text{Fe}(\text{HMDS})_2$ and dioxane from a 1:1:1 mixture in benzene.^[11] X-ray crystallography confirmed the bimetallic constitution of **1**, made up by two $\{\text{NaFe}(\text{HMDS})_3\}$ fragments connected via a Na-dioxane-Na bridge (see SI for details). Reacting 1,3-difluorobenzene with equimolar **1** at room temperature effected a colour change from a green to brown solution. Cooling this solution afforded heteroleptic $[(\text{dioxane})\cdot\text{NaFe}(\text{HMDS})_2(1,3\text{-F}_2\text{-C}_6\text{H}_3)]$ (**2**) in 67% yield. In **2** the aromatic substrate is metallated at its C2 position between the F substituents. Electrophilic interception of **2** with iodine affords 1,3-difluoro-2-iodobenzene **3a** in 84% yield (Scheme 1).

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In **2** Fe forms a σ bond at the 2-position of the aromatic ligand [Fe-C14, 2.1157(18) Å]; whereas Na interacts with one F [Na-F1, 2.3437(13) Å] (Fig 1).^[12] Both metals are also connected by an HMDS bridge. Fe completes its coordination sphere by bonding to a terminal HMDS, while Na is solvated by two dioxane molecules.

Emphasising the cooperativity between sodium and iron inherent in the reactivity of mixed-metal base **1**, neither homometallic Na(HMDS) or Fe(HMDS)₂ on their own can deprotonate 1,3-difluorobenzene (Scheme 1). Thus **2** can be regarded as a product of sodium-mediated ferration, with Fe actioning the deprotonation, but sodium being essential for this reaction to occur. Interestingly, it should also be noted that ferrated intermediate **2** is remarkably robust and does not decompose even when refluxed in C₆D₆ at 80°C for 24h.

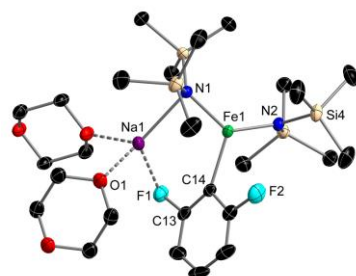
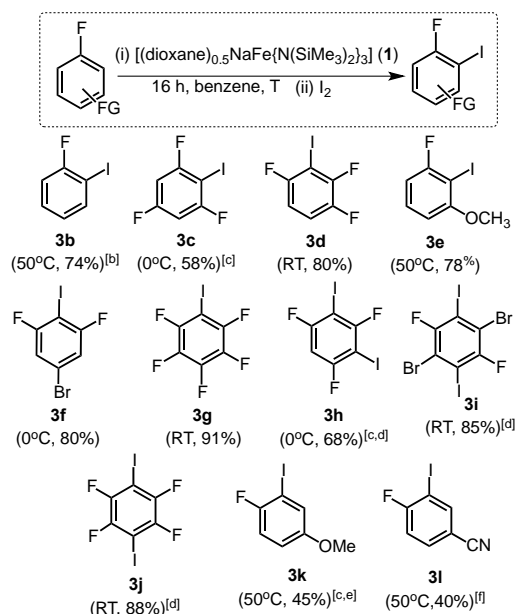


Figure 1 Monomeric, dinuclear structure of ferrate **2** with H atoms omitted for clarity and displacement ellipsoids displayed at 50% probability level.

Encouraged by this initial reactivity, we extended this approach to a range of fluoroaromatic substrates. Reactions were carried out in benzene, allowing mixtures to stir overnight prior to I₂ quenching (Table 1). Each metallation occurred at a position adjacent to at least one fluorine atom, affording iodo-fluoroarenes **3b–l** in good to excellent yields (40–91%). While Holland has reported that Fe(II) complexes can promote C–F bond activation processes when treated with perfluorinated arenes,^[13] here, selective Fe–H exchange reactions are observed. This C–H chemoselectivity also contrasts with previous studies using Fe(0) systems where C–F bond activation is usually preferred.^[14] Consistent with the different degree of C–H bond activation in the fluoroarenes studied,^[15] those substrates with only one F atom required harsher reaction conditions (50°C) (**3b**, **3e**, **3k** and **3l** in Table 1, 40–74% yields), whereas other Fe–H exchanges occur at RT or 0°C (**3c**, **3d** and **3f–3i** in Table 1, yields 58–91%). Interestingly, even in substrates possessing other *ortho*-directing groups such as 4-fluoroanisole or 4-fluorobenzonitrile, *ortho*-metallation at the F substituent is preferred (**3k** and **3l** in Table 1). These regioselectivities are opposite to those reported for lithiation of 4-fluoroanisole by ⁿBuLi in THF at –78°C^[16] or for 4-fluorobenzonitrile using related heterobimetallic (TMP)₂Fe·2MgCl₂·4LiCl.^[5] Contrasting with many lithiation reactions, where excess metallating reagent leads to complex mixtures of products,^[17] here stoichiometric control is seen as two equivalents of **1** regioselectively di-ferrate 1,3,5-trifluorobenzene, 1,4-dibromo-2,5-difluorobenzene and 1,2,5,6-tetrafluorobenzene, furnishing **3h**, **3i** and **3j** in 68, 85 and 88% yields respectively.

Interestingly, **1** failed to react with related chloroarenes, which also contain relatively activated H's, such as 1,3-dichlorobenzene, even under harsh conditions (50°C, 24h). This lack of reactivity contrasts with Schlosser's work using ^sBuLi at –100°C, where competition studies between this substrate and fluorobenzene show a clear preference for the former.^[18]

Table 1 Ferration of fluoroarenes using sodium ferrate **1**.^[a]



^[a] Reactions carried out with *in situ* prepared **1** in benzene. Unless otherwise stated, stoichiometric amounts of base and substrate and a five molar excess of iodine were used (see SI for details). Yields are of isolated products, see SI for details. ^[b] Fluorobenzene was used as solvent in the reaction. ^[c] Yield determined by ¹H NMR using ferrocene as internal standard. ^[d] Carried out using 2 equivalents of **1**. ^[e] 5 days, using 2 equivalents of **1**. ^[f] 2 days.

To shed more light on these intriguing findings, we next investigated key metallated intermediates **4a** and **4b** (Fig. 2), resulting from diferration of 1,3,5-trifluorobenzene and 1,2,4,5-tetrafluorobenzene prior to electrophilic interception.

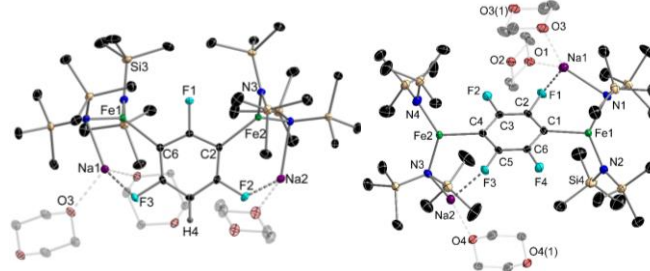


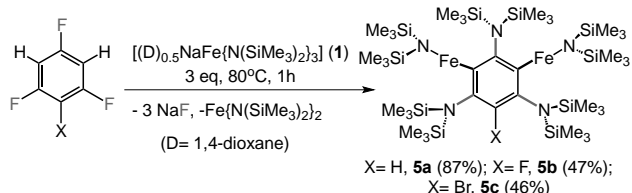
Figure 2 Molecular structures of complexes **4a** (left) and **4b** (right). Hydrogen atoms (except H4 in **4a**), minor disorder at one SiMe₃ in **4b** and a molecule of co-crystallised benzene solvent in **4a** are omitted for clarity. Displacement ellipsoids displayed at 30% probability level.^[19]

Both structures bear a strong resemblance to that of **2**, with the Fe centres occupying positions previously filled by H atoms (mean Fe–C distance, 2.110 and 2.134 Å for **4a** and **4b** respectively), whereas each Na atom binds datively with one F at the *ortho* positions (mean Na–F distance, 2.335 and 2.297 Å for **4a** and **4b** respectively). The distinct bonding preferences of

Fe and Na in these structures, tying up C and F lone pairs respectively, must contribute to the unusual room temperature stability of these potentially hypersensitive fluoroaryl dianions. Steric stabilization of the Fe-C bonds via the bulky HMDS groups is presumably another factor. As far as we can ascertain, **4a** represents the first structurally defined example of dimetallation of 1,3,5-trifluorobenzene whereas for 1,2,4,5-tetrafluorobenzene only two examples have been reported, though neither were made via direct metal-H reactions.^[20]

Previous studies of heterobimetallic amide bases such as alkali-metal zincates have shown that metallation regioselectivities can be influenced by coordination of the substrate to the alkali-metal prior to the metallation step.^[21] A similar scenario could be envisaged here, where initially the fluoroarene could coordinate to Na in **1** via a dative Na-F bond similar to those seen in **2**, **4a** and **4b**, bringing its adjacent H into close proximity to the anionically-activated ferrate {Fe(HMDS)₃} moiety, priming the intramolecular Fe-H exchange. Na...F interactions could therefore hold the key to the *ortho*-F selectivity/reactivity witnessed for all substrates studied (*vide supra*), whereas lack of such interactions could be a factor in the inertness of **1** with chloroarenes.

Exploring the ferrating limits of **1**, we next pondered if the three H atoms in 1,3,5-trifluorobenzene are exchangeable by Fe centres. Thus reacting the fluoroarene with excess **1** at 80°C (Scheme 2) gave a solution colour change from green to dark yellow and the formation of a precipitate. Cooling this solution gave yellow crystals of unimetallic iron complex [1,3-{Fe(HMDS)}₂-2,4,6-(HMDS)₂-C₆H] (**5a**) in 87% yield, where the fluoroarene has undergone an extraordinary 2-fold C-H/3-fold C-F activation, five bond-breaking process (Scheme 2).^[22] This approach could also be extended to 1,2,3,5-tetrafluorobenzene and 1-bromo-2,4,6-trifluorobenzene, furnishing bis(iron) compounds **5b** and **5c** (Scheme 2).



Scheme 2. Two-fold C-H/ three-fold C-F activation processes of 1,3,5 trifluorobenzenes.

The molecular structures of **5a-c** were established by X-ray crystallographic studies (see SI for full details and Fig. 3 for **5a**). Since **5a-c** are isostructural, only **5a** is discussed. Containing a 1,3-diferrated-pentasubstituted aryl ring, where each F atom of 1,3,5-trifluorobenzene has been replaced by HMDS, **5a** displays two low-coordinate Fe centres, each bonded to one C of the aromatic ring (mean Fe-C distance, 2.024 Å) and a terminal HMDS, adopting an unusual near-linear coordination (with C-Fe-N bond angles of 159.43(1) and 161.06(12)° for Fe1 and Fe2 respectively). Each Fe also forms a long-range contact with a neighboring HMDS attached to the aryl ring (mean Fe...N(HMDS)_{ring}, 2.389 Å). While these contacts are notably more elongated than those observed for HMDS groups directly attached to Fe (mean Fe-N distance, 1.919 Å), they are

significant enough to induce the distortion from linearity observed in the Fe geometries. It should be noted that two-coordinate iron (II) complexes are scarce in coordination chemistry, although they have already demonstrated unique magnetic properties.^[23] As far as we can ascertain **5a-5c** are the first dinuclear systems containing two pseudo-linear Fe centres to be structurally defined.

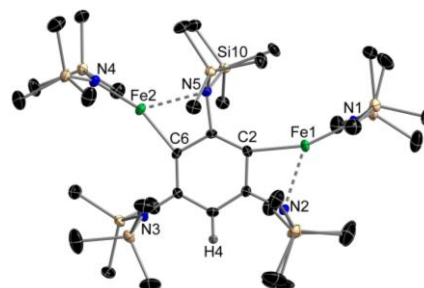
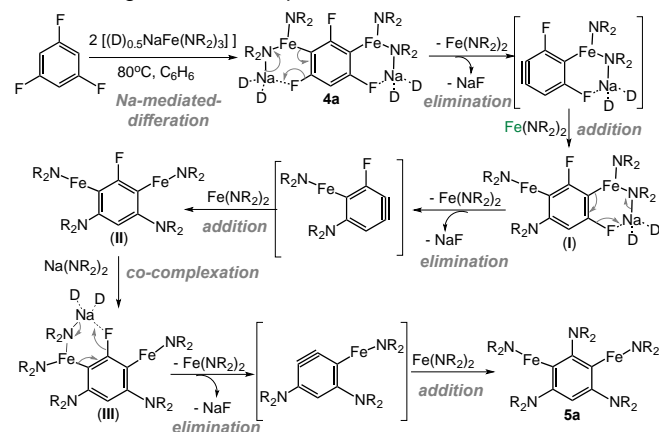


Figure 3 Molecular structure of **5a**. Hydrogen atoms (except H4) are omitted for clarity. Displacement ellipsoids displayed at 50% probability level.

While C-F bond activation of fluoroarenes by transition metals has been much investigated, to date, iron has shown limited promise in this area.^[8,12,14] It should also be noted that methods for C-F/C-N conversion are scarce, confined mainly to nucleophilic aromatic substitution of activated fluoroaromatics.^[24] Here, the synergic power of this Na/Fe bimetallic partnership allows conversion of three C-F fluoroarene bonds into three new C-N bonds as well as two direct Fe-H exchanges (Scheme 2). Filtrate analysis from the reaction of 1,3,5-trifluorobenzene and 3 equivalents of **2** showed the presence of Fe(HMDS)₂-(dioxane) complex and HMDS(H), while formation of precipitated NaF was confirmed by ¹⁹F NMR in D₂O. Furthermore, it was found that **5a** can also be prepared in excellent yield (90-95%) by treating diferrated product **4a** with one equivalent of sodium ferrate **1** or just one equivalent of Na(HMDS) at 80°C. Even more revealing, heating **4a** on its own in benzene for over an hour at 80°C also furnished **5a** albeit in a significantly lower yield (58%).

While this type of reactivity is unprecedented in transition-metal chemistry, Schlosser reported the conversion of 1,3,5-trifluorobenzene into 1,3,5-tris(tert-butyl)benzene using excess ^tBuLi via dilithiated aryl intermediates.^[9] Reflecting on that and our experimental findings, we propose that C-F bond activation products **5** form as a consequence of a cascade process, which takes place at 80°C. In a first step, diferration of the fluoroaryl (e.g. 1,3,5-trifluorobenzene in Scheme 3) by 2 equivalents of **1** will occur to form sodium ferrate **4a**. While this compound is stable at room temperature (*vide supra*), at 80°C it reacts to give **5a**, via an unstoppable domino of alternating NaF and Fe(HMDS)₂ eliminations and subsequent Fe(HMDS)₂ additions to benzyne intermediates. The existing Na...F contacts in **4a** may contribute to facilitate the activation of the relevant C-F bonds under these reaction conditions.^[25] Each diferrated intermediate should be less stable than its precursor (**III** > **II** > **I** > **4a** in Scheme 3), as this fast sequence of reactions does not stop until the three F atoms are replaced by HMDS groups, affording **5a**, where now the low-coordinate Fe centres are protected by bulky HMDS groups on the aryl ring.^[26] It should be noted that to

facilitate the last NaF/ Fe(HMDS)₂ elimination step (**III**→**5a**, Scheme 3), requires co-complexation of **II** with one Na(HMDS) equivalent. The sodium amide can be provided by a third equivalent of **1** (which explains the detection of Fe(HMDS)₂·(dioxane) complex with three equivalents of **1**), by some unreacted **4a** or by adding an extra equivalent of Na(HMDS) to **4a**. Interestingly, contrasting with these results, when diferrated intermediate **4b**, whose Fe centres reside at the 1,4-positions of the fluoroaryl anion, is reacted with an excess of **1** and heated at 80°C, no reaction was observed, hinting that the proximity of the Fe centres within the ring must also play a role in facilitating this activation process.



Scheme 3. Proposed cascade mechanism for formation of **5a** (D= dioxane, R= SiMe₃).

To conclude, by exploiting synergistic effects in sodium ferrate chemistry, we have unveiled a new regioselective method for the direct ferration of a wide range of fluoroarenes under mild reaction conditions as well as a novel type of C-F bond activation process. Isolation of metallated intermediates have shed light on how Na ions and Fe centres can cooperate in a synchronised manner to promote chemical transformations which neither sodium or iron amides are capable of facilitating on their own.

Acknowledgements

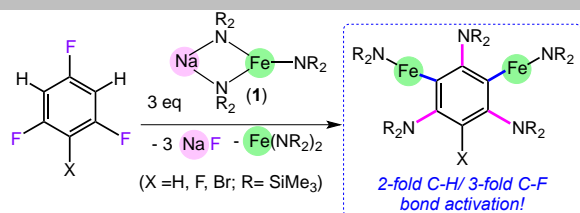
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Keywords: metallation, iron, mixed-metal chemistry; C-F bond activation, alkali-metals

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COMMUNICATION



High Five! Exploiting bimetallic cooperation, sodium tris(amido) ferrate **1** induces the collective cleavage of five (three C-F and two C-H) bonds of trifluoroarene substrates via a cascade activation process.

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